

Team-Based Thin-Film CIS Research Activities

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Abstract. This paper describes the team-based thin-film copper indium diselenide (CIS) research activities. The CIS team was formed in December 1994 in Kona, Hawaii. Originally, the team had two working groups: the "Junction" and the "Absorber" groups. Currently, there are four working groups: the Present Junction, New Junction, Substrate/Mo Impact, and Transient Effect groups. We have completed extensive data compilation of CIS-based films and solar cells using various techniques such as Auger, photoluminescence, scanning electron microscopy, secondary-ion mass spectrometry, X-ray photoelectron spectroscopy, X-ray diffraction, capacitance-voltage, light and dark current-voltage, and quantum efficiency. Studies are under way to understand the fundamental mechanisms that demonstrate a total-area, high efficiency of 17.7% in CuInGaSe₂ devices using chemical-bath deposition (CBD) CdS. Alternate buffer layers are also being investigated to replace the CBD CdS. The impact of various Mo substrates from the various industrial partners has been investigated, and the results are reported. A study is under way to investigate the transient effects in encapsulated/laminated thin-film CIS-based devices.

INTRODUCTION

The copper indium diselenide (CIS) team was formed as part of the Thin-Film Photovoltaics Partnership Program (TFPPP) in Kona, Hawaii, in December 1994. The TFPPP has two objectives. The first is to support the successful introduction of U.S. thin-film products by addressing key near-term technical issues at U.S. businesses committed to thin-film PV production. The second is to support advanced (mid- and longer-term) thin-film research and development needed by industry for future competitiveness, including module performance, cost per kWh, and reliability of thin-film photovoltaic (PV) technologies. As part of the teaming effort, about 35 members from industry, universities, and NREL are actively participating in the various working groups. Originally, there were two working groups (WGs), the "Junction" group and the "Absorber" group. Currently, there are four WGs: the "Present Junction (PJ)," "New Junction (NJ)," "Substrate/Mo Impact (SI)," and "Transient Effects (TE)." The WGs were increased from two to four to make the groups smaller (so that they could focus on their respective problems) and to keep the groups more manageable. Each WG decides its group's objectives and tasks. The working group

leader (WGL) is also selected by the WG. Also, ground rules have been established for all team members, and roles and responsibilities for the various personnel have also been established. Six team meetings have taken place at various locations in the United States.

Good working relationships have been established by the numerous members of the CIS team. The atmosphere has been one of collaboration with a spirit of cooperation, rather than a competitive atmosphere. Extensive data compilation for CIS-based films and devices has been completed and distributed among team members. Various characterization and measurement techniques such as Auger, photoluminescence (PL), scanning electron microscopy (SEM), secondary-ion mass spectrometry (SIMS), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), light and dark current-voltage, and quantum efficiency have been used to understand the fundamental mechanisms for CIS films and devices.

THE JUNCTION GROUP

The objectives of the CIS junction working group are to identify methods of forming junctions to CIS-based absorbers that are manufacturable, robust, and cost-effective, and to define diagnostic techniques and appropriate parameters to quantitatively compare junction quality. Toward this end, extensive experiments were planned and executed by the WG members. For example, a set of experiments decided by the WG members include the study of the surface and bulk compositions of absorbers, the chemical bath deposition (CBD) CdS/absorber interaction, the effect of CBD constituents and separate CBD reactants, physical vapor deposition, the CdS/absorber interaction, the CdS/I-ZnO interaction, the ZnO/absorber interaction (radiofrequency-sputtered ZnO), devices fabricated in all categories, and samples cut and distributed for analysis. Data were collected on the various films and devices and distributed to all the CIS team members. Figure 1 shows a PL plot of a CIGS film subjected to various surface treatments. The PL signal is strongest for the sample that has been CBD-CdS treated. The data indicate good electronic properties, presumably because of some surface passivation by the CBD process that results in a conformal coating on the CIGS film. Another possible explanation is that the CBD CdS acts as a diffusion barrier to the sputtered ZnO species.

THE ABSORBER GROUP

The objectives of the CIS/absorber fabrication, modeling, and diagnostics group are to establish a useful correlation between absorber properties, device modeling, and

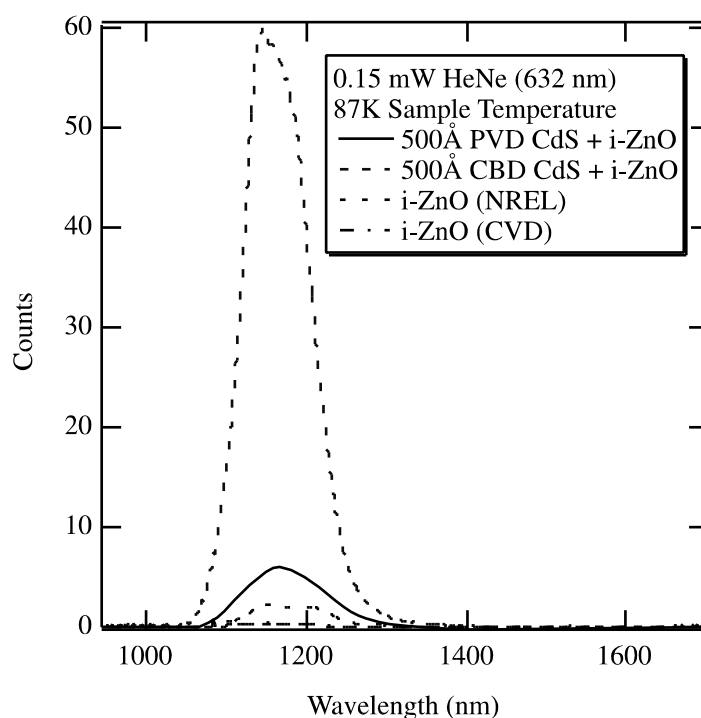


Figure 1. PL plots for four CIGS samples subjected to various surface treatments. The best PL signal is for the CIGS sample treated to a 500 Å CBD CdS and I-ZnO

actual device performance, and to develop "manufacturing friendly" material diagnostic tools that will lead to improved reproducibility and understanding of the physical and chemical nature of the absorber. The absorber group has two tasks. The first task is to identify the correlations between Ga and/or S profiles with the CIS-based absorber, the corresponding device performance, and performance predicted by modeling the equivalent device structure. This will be accomplished by participants fabricating CuInGaSSe_2 (CIGSS) absorbers, completing portions with CdS/ZnO/grids, and submitting it for film/device characterization. Characterization of the Ga and/or S profiles will subsequently be fed to device modeling, which will input measured Ga/S (bandgap) profiles into the code and compare the data to measured data. The second task is to correlate the chemical impurity content and structural nature of the absorber and absorber/back contact interface, and the device performance. This will be accomplished by participants fabricating CIGSS absorbers, completing portions with CdS/ZnO/grids, and submitting them for film/device characterization. Material characterization will target the identification of impurities that may originate external to the absorber, such as Na, K, and O, from the sodalime substrate, and the nature of the Mo/absorber interface after processing.

Figures 2a and 2b show the Auger depth profile for two Ga samples from International Solar Electric Technology (ISET) and Institutes of Energy Conversion (IEC) at the University of Delaware. The ISET sample shows a buildup of the Ga

content at the CIGS/Mo interface, whereas the IEC sample has a more uniform distribution over the entire CIGS layer.

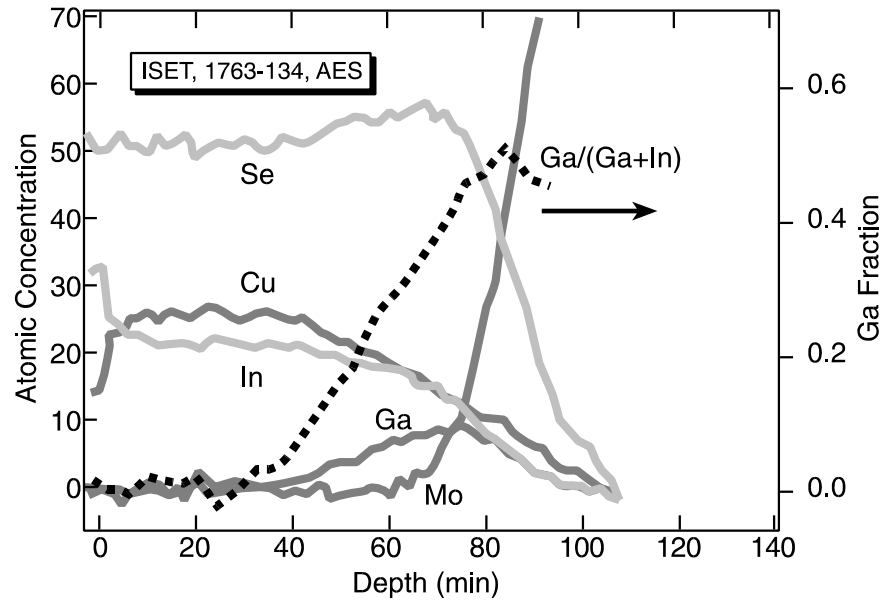


Figure 2a. Auger depth profile for an ISET CIGS absorber layer. The plot shows a build-up of the Ga at the CIGS/Mo interface.

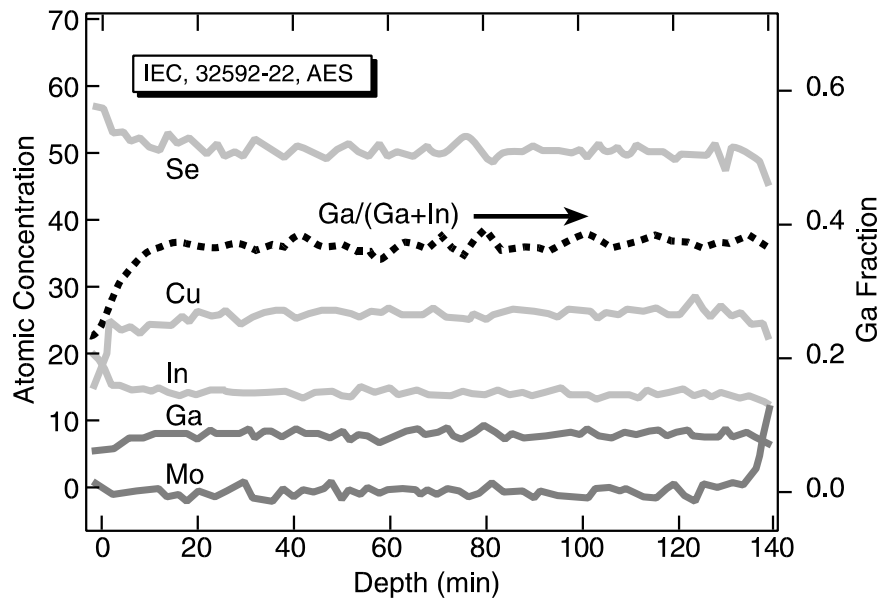


Figure 2b. Auger depth profile for a IEC CIGS absorber layer. The plot shows a more uniform distribution of the Ga in the CIGS absorber layer.

The effect of the Mo substrate was also studied. Mo substrates from six groups—Energy Photovoltaics (EPV), ISET, Lockheed Martin (LM), NREL, Siemens Solar Industries (SSI) and Solarex—were submitted to NREL. The CIGS absorber layer and device fabrication was done by NREL. Solar cell efficiencies varied from 4.3% to 17.3%. Extensive data have also been compiled by the Absorber group, and have been distributed to all team members.

REENGINEERING THE GROUPS

After completing the first year of team work, the Guidance Team decided that the WGs were too large and lacked sufficient focus. The Guidance Team therefore recommended smaller working groups with focused objectives and tasks. The new WGs formed are the PJ, NJ, SI, and TE groups.

Present Junction

The PJ is essentially a continuation of the earlier Junction group, but with fewer members. One common observation is that when a CBD CdS film is used as a buffer layer between the CIGS absorber layer and the I-ZnO layer, one gets the world-record, total-area solar cell efficiency of 17.7% verified by NREL. The exact role of the CBD CdS is not entirely clear. Some researchers have speculated that the CBD CdS acts as a passivating layer by forming a conformal coating on the CIGS absorber layer, which in turn reduces the surface recombination velocity and improves the device performance. Others have argued that the CBD CdS buffer layer acts as a diffusion barrier to the various ZnO species during the sputtering process.

The objective of the PJ WG is to understand the mechanisms by which CdS, especially CBD CdS, makes the most efficient CIS junction, and to compare the relative merits of different CdS deposition techniques.

New Junction

There is an apparent consensus in the CIS community that the very thin CdS (500 Å) buffer layer needs to be replaced by a noncadmium containing layer to give the technology a "green" (environmentally friendly) appearance. Toward this end, there is a great deal of research under way in Japan, Germany, and the United States to replace the CBD CdS by other candidates, such as $\text{In}(\text{OH})_2$, In_2S_3 , SnO_2 , ZnO, ZnSe, or ZnS. However, to date, the use of these alternate buffer layers has resulted in lower cell efficiency. NREL, in collaboration with Washington State University (WSU) has

fabricated a CIGS solar cell without any CdS buffer layer, having a total-area efficiency of 12.7%. WSU researchers deposit the I-ZnO by metal organic chemical vapor deposition.

Another concern of the PV industry is the ZnO transparent conducting oxide (TCO). In a CIS module, the typical thickness of the ZnO layer is 2.0 to 2.5 μm to get the appropriate sheet resistance of about 8 ohms/sq. The lower sheet resistance is necessary to get lower series resistance and higher fill factor in a module. As the thickness of the ZnO increases, the amount of sunlight the cell absorbs decreases because of the optical losses in the ZnO. One of the challenges for this WG is to reduce the thickness of the ZnO layer while getting lower sheet resistance and higher transmission. In addition, it has been observed that the electronic and optical properties of ZnO deposited on sodalime glass are not the same as those when ZnO is deposited on the CIGS absorber layer. The NJ WG group is addressing these research issues.

The NJ WG has two objectives. The first objective is to develop noncadmium-containing buffer layers. The priority will be on vacuum processes that could potentially be incorporated into in-line manufacturing. CBD is not considered a primary option. The second objective is to develop improved TCO layers to minimize losses for module fabrication and quantify the effect of TCO layers on module performance. This task will focus only on the high-conductivity TCO layer.

Substrate Mo/Impact

The previous Absorber WG conducted a set of experiments to evaluate the role of the Mo contact on the device performance. Six Mo substrates from the various industrial partners and NREL were part of this WG experiment. The CIGS was deposited by NREL, and device fabrication was also done by NREL. The solar cell efficiency varied from 4.5% to 17.3%, thus indicating a strong dependence on the Mo substrate and that not all Mo is created equal.

Another impact of the substrate is the out-diffusion of Na from the low-cost sodalime glass substrate through the polycrystalline Mo films and into the CIGS absorber layers. Thus far, Na has had a positive impact on the device performance. Scientists have argued that Na enhances the grain growth, acts as a dopant, improves the carrier concentration, and thus improves device performance. Although considerable empirical evidence exists, the exact role of Na is unclear. This becomes all the more important if alternate substrates such as alumina, polyamide, or stainless steel are used, because in these cases the extrinsic addition of Na is required to enhance device performance. Adding a diffusion barrier such as SiO_2 between the glass and Mo contact has been investigated thus far.

The objective of this WG is to study the impact of the glass substrate and Mo contact on the performance of CIS-based solar cells. The research includes correlation of Mo properties (chemical, mechanical, and structural) and the degree of Na diffusion through the layer; the study of substrates/Mo/CIS interaction through sample exchange between WG partners; and the possible diffusion barriers for Na.

Transient Effects

Substantial development work done by Siemens Solar Industries to encapsulate/laminate CIS-based mini-modules has indicated an initial drop in the mini-module performance after encapsulation/lamination. However, when exposed to natural sunlight for a few weeks, the mini-modules regain or exceed initial performance. This effect is shown in Figure 3, and is the topic of investigation for the TE WG.

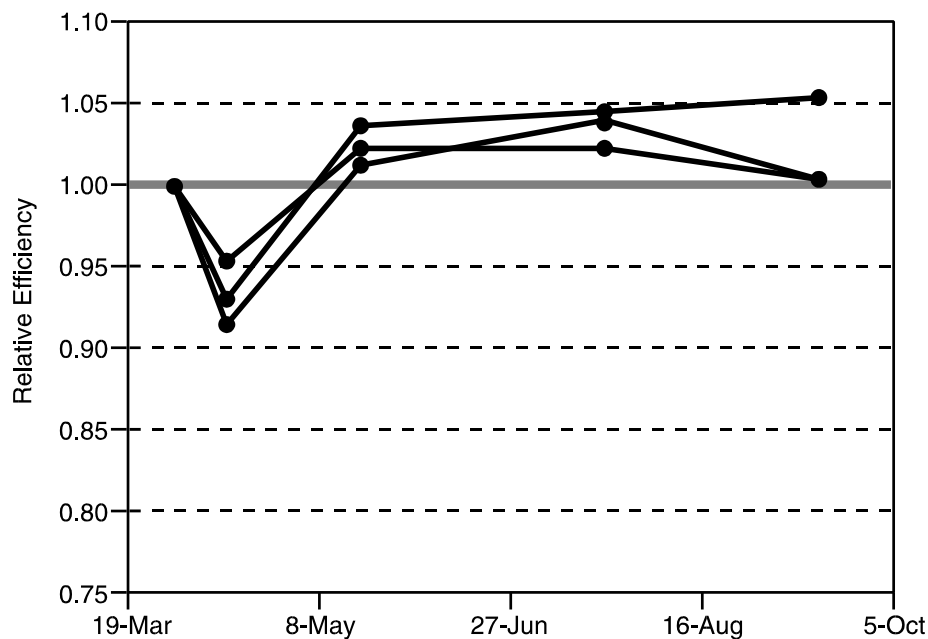


Figure 3. This plot shows the transient effects of a CIGSS mini-module fabricated by SSI after encapsulation/lamination and then exposed to natural light.

The objective of this WG is to study the transient effects in thin-film CIS-based devices. Studies will include solar cells, mini-modules, and modules before and after encapsulation/lamination. Major emphasis will be on understanding the fundamental mechanisms responsible for these effects in CIS-based devices.

SUMMARY

The CIS team was established in December 1994. Since then, substantial technical progress has been made in better understanding the film and device properties of CIS. Extensive data using various techniques (Auger, PL, XPS, XRD, SEM, and SIMS, for films and; dark and light I-V, quantum efficiency, and capacitance-voltage for solar cells) have been compiled and distributed among the team members. There have been several exchanges of samples between team members. Discussions at team meetings have been candid, and there is a healthy spirit of cooperation among the team members. Working groups have been reengineered, so that smaller WGs focus on research problems that will help the PV industry solve relevant technical problems to commercialize thin-film CIS technology.

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